Upgrading a High Asphaltene Content Petroleum Residue by Hydrogenation with a NiMo-supported Catalyst

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INTRODUCTION

Upgrading petroleum heavy fractions has been increasingly important in petroleum refining for both economic benefit and environmental protection. Many technologies and strategies are now available for upgrading heavy residua. These processes can be divided into two broad categories: carbon rejection and hydrogen addition[1]. Carbon rejection processes redistribute hydrogen among the various components, resulting in fractions with increased or decreased H/C atomic. On the other hand, hydrogen addition processes involve external addition of hydrogen and result in an overall increase in H/C ratio of the products compared to that of the starting feedstocks. Hydroprocessing with NiMo (or CoMo)-supported catalysts has been widely used in commercial units because of high yields of liquid products and heteroatom removal[2-4]. Various heavy fractions have been used as feedstock for hydroprocessing. Process conditions depend on two major factors: feedstock properties and product specifications.

Catalyst deactivation in hydroprocessing is considered an important part of the process cost. Many deactivation processes, such as blocking of active sites by adsorption of asphaltenes, coke formation on the catalyst surface, pore blockage caused by metal accumulation, were researched[5,6]. Asphaltenes are considered to be responsible for the initial deactivation of the catalysts in heavy oil hydroprocessing[7,8], because of their adsorption on cobalt (or nickel) and molybdenum oxides and sulfides. At relatively high temperatures, asphaltenes are transformed to coke which deposits on the catalyst surface and causes deactivation of the catalysts. Therefore, the removal of asphaltenes is important for inhibiting catalyst deactivation and improving the downstream operating severity in a refinery.

Hydrogen-carbon atomic ratio (H/C) of feedstock is one of important factors determining the operation conditions. High H/C ratio means the feedstock has high hydrogen saturation and can be processed at relatively severe operation conditions. The change in H/C atomic ratio during the upgrading process can be used to measure the hydrogenation activity of a catalyst.

The present work explores the effects of a NiMo-supported catalyst and reaction conditions on upgrading a petroleum heavy residue, a ROSE pitch, which has high asphaltene and sulfur contents. Specifically, asphaltene conversion, sulfur removal, change in H/C atomic ratio, coke formation, and distillate production were investigated.

EXPERIMENTAL

The properties of the ROSE pitch used in the present work are listed in Table 1. The asphaltene and sulfur contents of the pitch are 29, and 6.0 wt%, respectively, and its H/C atomic ratio is 1.27. A simulated distillation analysis showed that the vacuum residue fraction (b.p.>525 °C) comprises more than 95 wt% of the pitch. A commercial catalyst, $NiMo/SiO_2-Al_2O_3$, was used hydrogenation experiments. The catalyst was sulfided in a batch reactor with CS_2 (anhydrous, > 99 %) as sulfur agent in *n*-dodecane (anhydrous, > 99 %) in two temperature stages: 200 °C for 2 h, and, then ,350 °C for 3 h before it was used in the experiments.

Reactions were carried out in 316 stainless steel batch reactors (25 mL) heated in a fluidized-sand bath. After adding the pitch and the catalyst, the headspace gas in the reactor was replaced three times with hydrogen before the reactor was charged with hydrogen to the desired cold pressure. Then, the reactor was plunged into a preheated sand bath. The experiments were carried out in the following range of conditions: 375 to 425 °C, initial H_2 pressure of 600-1250 psig, catalyst concentration of 10 - 20 wt%, and time periods of 30 – 90 min. The reactor contents reached the desired reaction temperature within 3 minutes. At the end of the reaction, the reactor was quenched in cold water. Liquid products (THF soluble) and solids (catalyst and deposited coke, THF insoluble) mixtures were washed with THF (Tetrahydrofuran, purity > 99.9 %). After separation of the solids from the mixture, the liquid products were recovered by evaporation of THF.

Asphaltene contents of the pitch and the liquid products were measured by treating the samples (0.2 ± 0.02 g) with n-hexane (20 mL) in an ultrasonic bath for 5 minutes, followed by settling for another 10 minutes before vacuum filtration through a previously weighed GF/A filter paper. The filtration residue was washed with excess hexane (about 30 mL). The solid residue and vial (as some residue remains adhered to the vial surface) were dried in a vacuum oven and weighed to determine the asphaltene content of the sample. The H/C atomic ratio and sulfur content of the feedstock or liquid products were measured by CHN–600 elemental analyzer and LECO sulfur analyzer, respectively. The coke on the catalys was defined as the difference in weight between the solid products (THF insoluble materials and catalyst) and the fresh catalyst. The fractional distribution of liquid products with repect to boiling point ranges was determined by Simulated Distillation gas chromatography (Hewlett Packard Series II 5890) with a high-temperature Megabore column P/N SD-002 HTC and a flame ionization detector.

RESULTS AND DISCUSSION

In order to investigate the effect of the catalyst on asphaltene conversion, the experiments were carried out either with or without the catalyst, but in the presence of hydrogen at the same initial pressure for both reaction systems. As shown in Figure 1, in the absence of the catalyst, both at 400 and 425 °C, the asphaltene conversion showed negative values, indicating an increase in asphaltene content after thermal reactions. In the same reaction system, the H/C ratio also decreased from 1.27 for the feedstock to 1.20 for the liquid products. The coke formation increased from 2 wt% of the feedstock at 400 °C to 10 wt% at 425 °C, as shown in Figure 2.

When the catalyst was present in the reaction system, both the asphaltene conversion and the H/C atomic ratio of the products increased. An asphaltene conversion of 44 and 46 wt % was achieved at 400 and 425 °C with the liquid product H/C of 1.35 and 1.37 at the corresponding reaction temperatures, respectively. These results are attributed to hydrogenation activity of the catalyst. The catalyst also showed high hydrodesulfurization (HDS) activity and suppressed coke formation (Figure 2). At 425 °C, more than 65 wt% sulfur was removed from the liquid products with only 1.5 wt% of the feedstock transformed to coke, compared to approximately 10 wt% coke obtained without the catalyst.

Figure 3 shows the change in asphaltene conversion and H/C ratio with increasing the temperature from 375 to 425 °C for 45 minute reaction. A significant increase in both parameters was observed upon increasing the temperature from 375 to 400 °C, with slight changes upon further increase in temperature from 400 to 425 °C. It appears that the thermal reactions, e.g., cracking and polymerization, become significant enough above 400 °C to offset the increase in hydrogenation activity of the catalyst. With the increasing reaction temperature from 375 to 425 °C, sulfur conversion increased proportionally from 13.5 to 45.7 wt %, and coke formation increased from 0.58 to1.3 wt%, as shown in Figure 4.

Figure 5 shows the effect of hydrogen pressure on asphaltene conversion and H/C ratio at 425 °C for 90 min with a catalyst concentration 20 wt %. Both parameters increased almost linearly with the increasing cold hydrogen pressure from 600 to 1250 psig. An asphaltene conversion of 92 wt% and a H/C ratio of 1.51 were achieved at the highest pressure used in the experiments. High hydrogen pressure also promoted sulfur removal, as shown in Figure 6, but it did not affect the coke formation to any significant extent in the range of 600-1250 psig initial H_2 pressure.

Increasing the reaction time from 30 to 45 min increased the asphaltene conversion from 31 to 46 wt% at 425 °C, 1000 psig initial H_2 pressure and 10 wt % catalyst concentration. Further increase in reaction time to 90 min did not cause any significant change in asphaltene conversion or in the H/C ratio of the liquid products. These observations can also be explained by the competing catalytic and thermal reactions, as discussed before for high temperature experiments.

Figures 7 shows the simulated distillation curves of the liquid products as a function of reaction temperature at 1000 psig initial hydrogen pressure, 45 min and 10 wt % catalyst. The distillation curve for the starting residue is also shown in Figure 7 for comparison. With the increasing reaction temperature, the curve shifts to lower temperatures, indicating the production of lower boiling-point material. The conversion of 525 °C⁺ fraction was 5.2, 12.2 and 35.5 wt% at 375, 400 and 425 °C, respectively. The conversion increased nearly three times when the reaction temperature increased from 400 to 425 °C. Increasing the reaction time to 90 min at 425 °C (not shown in the figure) gave approximately 50 wt% conversion of the 525 °C⁺ fraction. This means that thermal reactions essentially controlled the cracking at higher reaction temperatures.

CONCLUSIONS

Hydrogenation of a ROSE pitch produced liquids with low asphaltene and sulfur content and high H/C atomic ratio because of the high hydrogenation activity the NiMo-supported catalyst used in this work. At both low and high reaction temperatures, the hydrogenation activity of the catalyst was predominantly responsible for the asphaltene conversion and increase in the H/C atomic ratio. High extents of sulfur removal and suppression of coke formation were also possible because of the high hydrogenation activity of the commercial catalyst.

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Table 1. Properties of ROSE Pitch Feedstock

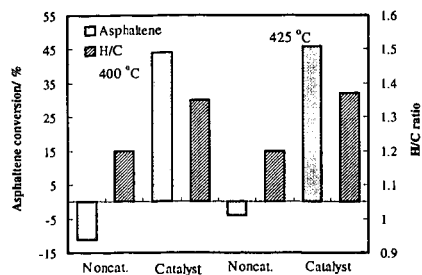| Simulated distillation, wt %	
naphtha (IBP - 171 °C)	0.0
kerosene (171 - 232 °C)	0.0
gas oil (232 - 370 °C)	0.7
VGO (370 - 525 °C)	3.7
residue (525 °C+)	95.6
Asphaltene, wt %	29
Elemental analysis, wt %	
C	82.4
H	8.7
N	0.61
S	6.0
H/C atomic ratio	1.27

Figure 1. Comparison of thermal and catalytic reactions in asphaltene conversion and H/C atomic ratio change. 1000 psig H_2 pressure; 90 min; 10 wt % catalyst.
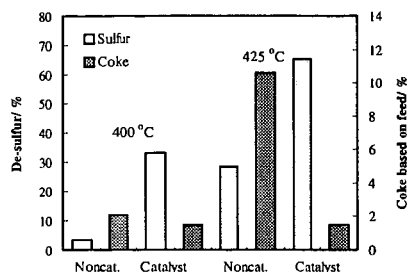

Figure 2. Comparison of thermal and catalytic reactions in sulfur conversion A nd coke deposits. 1000 psig H_2 pressure; 90 min; 10 wt % catalyst.
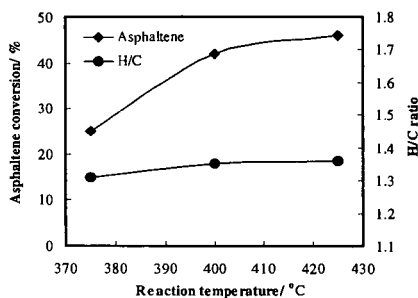

Figure 3. The effect of reaction temperature on asphaltene conversion and H/C atomic ratio increase. 1000 psig H_2 pressure; 45 min; 10 wt % catalyst.
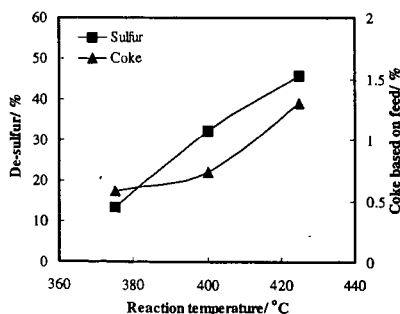

Figure 4. The effect of reaction temperature on sulfur conversion and coke deposits. 1000 psig H_2 pressure; 45 min; 10 wt % catalyst.
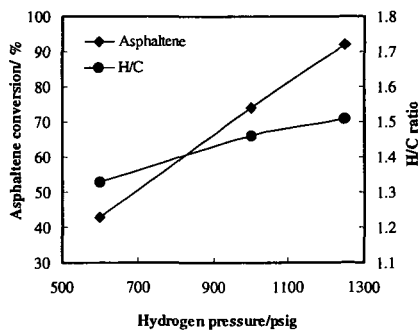
Figure 5. The effect of initial H_2 pressure on asphaltene conversion and H/C atomic ratio increase. 425 °C; 90 min; 20 wt % catalyst.
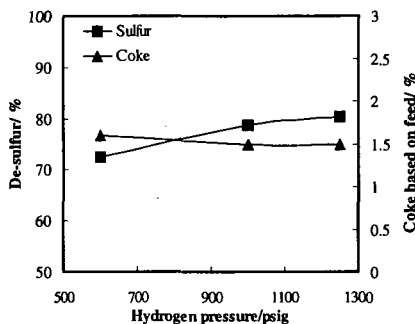

Figure 6. The effect of initial H_2 pressure on sulfur conversion and coke deposits. 425 °C; 90 min; 20 wt % catalyst.
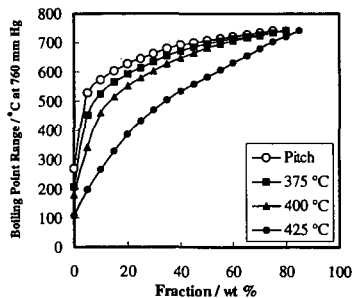

Figure 7. Distillation curves of feedstock and products at different reaction temperature. 1000 psig H_2 pressure; 45 min; 10 wt % catalyst.